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SOME FUNDAMENTAL MEASUREMENTS ON FISCHER TROPSCH CATALYSTS.

J.M. Roxburgh.

April, 1947

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J.M. Roxburgh, B.Sc. in Chemical Engineering

entitled:-

SOME FUNDAMENTAL MEASUREMENTS ON
FISCHER TROPSCH CATALYSTS

Measurements of the surface areas of various catalysts and supporting media and of the rates of certain reactions taking place on these catalysts.

Professor

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SOME FUNDAMENTAL MEASUREMENTS ON FISCHER TROPSCH CATALYSTS.

Measurements of the surface areas of various catalysts and supporting media and of the rates of certain reactions taking place on these catalysts.

Submitted in Partial Fulfillment
of the
Requirements for the Degree of
MASTER OF SCIENCE
by
J.M. Roxburgh, B.Sc.
under the direction of
Dr. S.G. Davis

Time devoted to thesis work represents the equivalent of three full courses.

University of Alberta,
Department of Chemistry,
Edmonton, Alberta.

April, 1947

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INTRODUCTION.

The development of catalysts useful in the synthesis of hydrocarbons and related products from mixtures of carbon monoxide and hydrogen has been, until recent years, a purely empirical study. No fundamental knowledge of the requirements for a good catalyst was available and a method of trial and error had been used exclusively in the early work of Fischer and co-workers[8].

Not only the composition of the catalyst and the supporting medium but also the conditions of pressure, rate of gas flow, and indeed the whole synthesis procedure as first evolved was based on purely empirical data.

On this basis, several practical, though probably uneconomic, plants were built in Germany. However, before English and American capital could be interested in similar plants, more fundamental knowledge of the process was necessary. Cost and efficiency factors which the Germans could afford to ignore in their great need for hydrocarbon fuels could not be ignored by companies which must compete both with crude oil and with other possible synthesis processes.

With this incentive many investigations have

been pursued in recent years. These studies have not been directed towards finding new catalysts in general but rather towards obtaining a better understanding of the catalysts already known.

These investigations may be roughly divided into three classifications:-

1) Fundamental studies directed towards an understanding of the mechanism of the reaction and the parts played by the various promoters and supporters.
2) Pilot plant work to determine the optimum conditions under which the synthesis should be run.
3) The chemical engineering problems of reactor design, cooling systems, recycling processes, etc., on a pilot plant scale.

These three types of studies are, of course, very closely interdependent and correlation between them must be maintained.

The work carried out by Boomer and others at the University of Alberta has been primarily aimed at determining the activity of various catalysts and the conditions under which they will operate most sat-

isfactorily. A great deal of time was expended on catalysts which in the end proved unsuitable due either to low activity or short life. This only became apparent after a rather long period of testing in the pilot plant reactors. One of the aims of this investigation is to evolve a method of testing based on fundamental properties of the catalysts that would show in a short test the approximate capabilities of a particular catalyst as to activity and life. It was hoped that these studies might also throw some light on the mechanism of the reaction.

THE THEORY OF ADSORPTION.

The phenomenon of adsorption, the concentration at the interface of molecules dispersed in one of the phases, has been known and studied for many years. C.W.Scheele in 1773 and Abbé F.Fontana in 1777 observed that gases were adsorbed on charcoal, but it was not until about 1915 that any satisfactory picture of adsorption, based on a fundamental mechanism, was advanced.

The amount of adsorption occuring at equilibrium, "a", is known to be a function of temperature and pressure (or concentration, if adsorption takes place from solution). The equation for the isotherm is, then,

$$a = f(P) \;\ldots\ldots\ldots\; (T \text{ constant})$$

for the isobar,

$$a = f(T) \;\ldots\ldots\ldots\; (P \text{ constant})$$

and for the isotere,

$$P = f(T) \;\ldots\ldots\ldots\; (a \text{ constant})$$

Empirically it was early discovered that at low pressures the equation for the isotherm became

$$a = kP$$

which is analagous to Henry's Law for the solubility of gases in liquids.

At higher pressures it is necessary to write

$$a = kp^{1/n}$$

where "n" is greater than one. The factor "n" is not constant over any large pressure range. This equation for the isotherm was first proposed by Bemmelen in 1888 but is usually referred to as the Freundlich isotherm since he revived it in 1922. This equation expresses satisfactorily the adsorption of a gas over a small range of pressure but has no fundamental significance. It is particularly useful as an interpolation equation where it can be made to fit the experimental data.

Several modifications of the Freundlich isotherm have been proposed. Arrhenius gave

$$\frac{dx}{dc} = \frac{k(s - x)}{x}$$

where "s" is the saturation value of "x", the amount adsorbed. This also only applies over a very short range of pressure in most cases. Schmidt proposed

$$\frac{dx}{dc} = k(s - x)$$

earlier, and later modified this to

$$xe^{A(s-x)/s} = kcs$$

which agreed well with experimental results in a great

many known cases.

All of these were empirical expressions. In 1914 two different theories were advanced, both with some fundamental basis. Langmuir proposed an isotherm based on the assumption that adsorption involved forces of the nature of the chemical bond, and that the adsorbed layer was consequently only one molecule thick. Polyani on the other hand believed that adsorption was purely physical in nature and that the adsorbed phase was many layers thick.

Langmuir made three assumptions as the basis for his derivation:-

(1) that the attraction between the molecules is less than the attraction between a molecule and the adsorbing surface

(2) that the probability of evaporation of a molecule from the surface is the same whether the neighboring positions are filled or not

(3) that molecules striking adsorbed molecules are elastically reflected and only those striking the bare surface have a chance to be adsorbed.

With these assumptions the isotherm

$$x = \frac{abP}{1 + aP}$$

can be derived kinetically as Langmuir did it, thermodynamically or statistically.

This isotherm, where it is applicable, will fit the experimental data from low to high pressures.

Polyani did not derive an actual isotherm equation. Starting with the assumption that the adsorbed gas acts as a compressed film on the surface and obeys the same equation of state as in the gas phase, he derived equations for expressing ϵ, the potential, as a function of φ, the volume adsorbed. The ϵ, φ curve is independent of temperature. It can be plotted from one experimentally determined isotherm and other isotherms then plotted from it. Although the physical concept of adsorption upon which this theory is based has been discarded, it does correctly express the temperature dependence of adsorption for the systems to which it is applicable.

Zsigmondy in 1911 proposed a theory of capillary condensation to account for adsorption. It is known that the vapour pressure of a liquid in a

capillary is lower than that in the bulk phase if the liquid wets the capillary walls. It is also known that many adsorbent materials have pores of minute size, so that it is logical to assume that this capillary condensation does play some part in adsorption.

Patrick, in 1920, approached this theory empirically. A variation of the Freundich equation was used

$$v = k(P/P_o)^{1/n}$$

where P_o is the vapour pressure of the liquid. Others based their approach on the extrapolation of the Kelvin equation to the small radii of capillaries present in adsorbents. When the capillaries are not too fine and the relative pressure, P/P_o, is approaching unity the isotherms are successfully represented by the equations thus derived. In other cases capillary condensation plays a relatively unimportant role.

DeBoer and Zwicker in 1929 proposed a polarization theory to account for multimolecular adsorption, assuming that adsorbed molecules were polarized and could adsorb a further layer, polarizing these molecules in turn.

The equation

$$\text{Ln } P_n/K_3P_o = K_2{K_1}^n$$

was derived, where "n" is the number of layers.

Emmett and Brunnauer[6] showed that the polarization theory cannot account for more than a small part of the energy holding even a second layer of molecules, particularly with such gases as argon.

Brunnauer, Emmett and Teller in 1938 proposed a theory of multimolecular adsorption which is now generally accepted as a good approximation in most cases. They derived the isotherm equation

$$(P/v).(P_o-P) = (1/v_mC) + \frac{C-1}{v_mC}.\frac{P}{P_o}$$

where v is the volume of gas adsorbed

v_m is the volume of gas to form a unimolecular layer over the whole surface of the adsorbent.

P is the equilibrium pressure.

P_o is the vapour pressure of the liquid.

C is a constant characteristic of the system.

The values of C and v_m are obtained from the slope and intercept of the straight line plot of P/P_o against $(P/v).(P_o-P)$. The surface area of the adsorbent can be calculated from a knowledge of the size of the

adsorbed molecule.

This derivation is based on the assumption that the same forces are operative in adsorption that cause condensation. It is in effect a generalization of Langmuir's treatment of monomolecular adsorption and contains the same assumptions.

Five types of adsorption isotherm are described by Brunnauer[1]. Of these, the B.E.T. equation as given previously describes adequately three types. A somewhat more complex treatment is necessary for the other two types, taking into account the effect of capillary condensation.

These five types of adsorption isotherm are shown in Figure I. Type I is characteristic of monomolecular adsorption, that is, the Langmuir isotherm. A saturation adsorption corresponding to a unimolecular layer is reached at a pressure less than the vapour pressure of the liquid. This is a special case of the B.E.T. general equation, which may be simplified to

$$v = \frac{v_m(C/P_o)P}{1+(C/P_o)P}$$

for this type of isotherm. This is an expression of the Langmuir isotherm equation.

Five Types of Adsorption Isotherms.

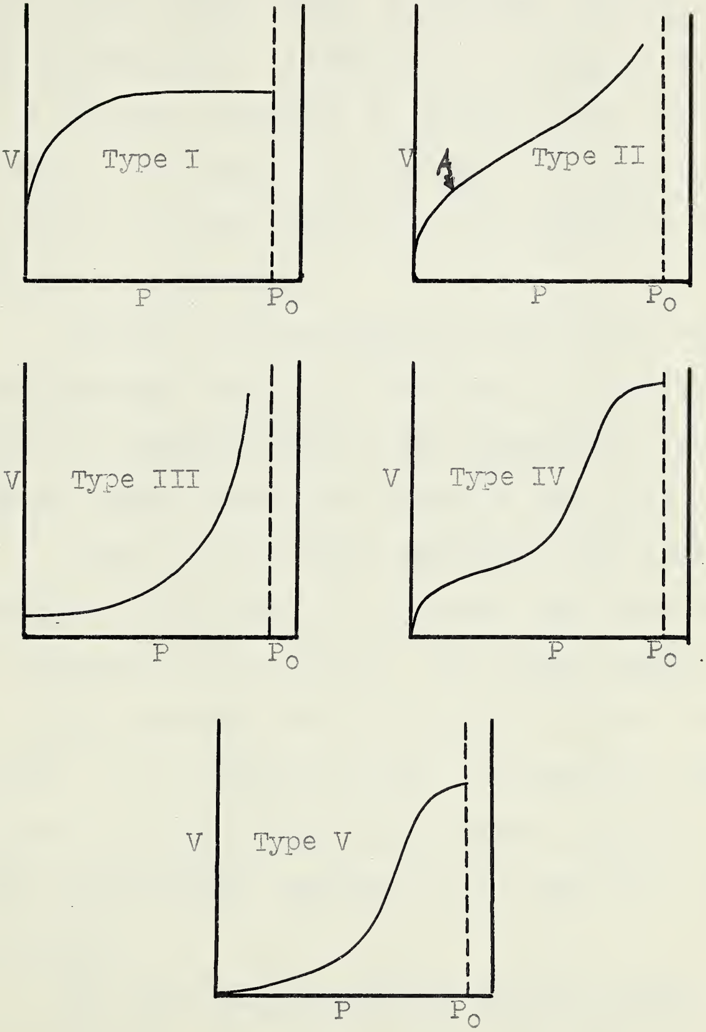


FIGURE I

Type two isotherm is characteristic of multimolecular adsorption where E_I, the average heat of adsorption of the first layer, is greater than E_L, the heat of liquefaction. In this case a complete first layer of adsorbed molecules is formed on the surface before second and higher layers begin to condense. The point "A" on the curve indicates the completion of the first layer of molecules.

When E_I is less than E_L, the plot of the adsorption isotherm takes the form shown in Type III. This type is characterized by the formation of second and higher layers before the first is completed.

Types IV and V show evidences that capillary condensation is occuring at pressures less than the vapour pressure of the liquid. The simple expression of the B.E.T. equation does not apply to these rather rare cases. The equation derived by Brunnauer, Emmett and Teller for these cases is much more complex and involves three further assumptions in addition to those already used:-

(1) That the capillaries are of uniform size

(2) That the walls of the capillaries are plane parallel surfaces

(3) That the capillaries are open on the sides.

As pointed out by Brunnauer[1], this theory is open to some criticism. When P/P_0 is small, it reduces to the Langmuir isotherm and since the adsorbing surface is heterogeneous, the assumption that E_I is constant over the surface is not valid. At higher values of P/P_0, E_I will be more nearly constant. The agreement is found to be good with experimental results over the range $0.5 > P/P_0 > 0.05$ for the types of isotherm to which the equation applies. At higher values of P/P_0 capillary condensation plays an important role and must be taken into account. At temperatures above the critical temperature for the adsorbate the assumptions used break down and the equation is not applicable. It is probable that only unimolecular adsorption occurs in this range.

All these investigations and the resultant equations apply only to Van der Waal's adsorption, that is, where the attraction is physical in nature. In activated adsorption, or chemisorption as it is sometimes called, different forces come into play and these derivations do not apply.

THE MEASUREMENT OF SURFACE AREAS.

When the adsorption isotherm is of Type I, (Fig. I) the evaluation of the surface area can be carried out by means of the special case of the B.E.T. equation noted previously, which is the Langmuir isotherm. If we write this equation in the form:-

$$P/v = 1/(v_m b) + (P/v_m)$$

it is obvious that a plot of P/v against P will be a straight line of slope $1/v_m$. The surface area can be calculated if the size of the adsorbed molecule is known.

Certain precautions are necessary in the choice of experimental conditions in order that v_m should represent a monomolecular layer over the whole surface and not just the more active parts. The adsorption should be measured at pressures close to the vapour pressure at any particular temperature, which means in most cases working at temperatures only slightly higher than the boiling point at atmospheric pressure.

When the isotherm is of Type II, the B.E.T. equation applies. The best range of application is at a relative pressure of from 0.1 to 0.4. Again we

should be working at a temperature only slightly above the boiling point. If P/P_0 is plotted against $\frac{P}{v(P_0-P)}$ a straight line will be obtained. From the intercept, $1/(v_mC)$, and the slope, $(C-1)/(v_mC)$, the value of v_m, and hence the surface area, is obtained.

The size of the measuring molecule is of great importance in the measurement of surface area. The surface area obtained will vary to a certain extent with the measuring molecule, since some larger molecules will be excluded from the smaller capillaries which are open to the smaller molecule.

Emmett and DeWitt[7], using this method, have reported excellent agreement in several hundred experimental determinations, checking their results by using different measuring gases. Ultramicroscope measurements also give values in good agreement.

In the majority of cases it is satisfactory to take only one or two measurements of adsorption, corresponding to a relative pressure of about 0.4. When C is large, the slope of the line joining this one point to the origin in the plot of P/P_0 against $P/v(P_0-P)$ is $1/v_m$ within the limits of experimental

error, since (C-1) and C are approximately equal and the intercept, $1/v_mC$ will be negligibly small.

In this investigation, all surface areas were measured using nitrogen as the adsorbed gas at a temperature of 83° K. At this temperature the vapour pressure of liquid nitrogen is 158 cm. of Hg so that pressures between 15 and 70 cm. of Hg are in the useful range of relative pressures of from 0.1 to 0.4.

It has been suggested that the surface area of a catalyst for the Fischer-Tropsch reaction should be, in some degree at least, a measure of the activity. This investigation indicates that surface area is not a controlling factor, but it is assumed that a certain minimum area is necessary for an efficient catalyst.

THE MECHANISM OF THE SYNTHESIS REACTION.

The most widely accepted theory for the mechanism of hydrocarbon synthesis on cobalt-thoria-keiselghur catalysts is that of Craxford and Rideal[2,3]. Several steps are postulated leading to the eventual formation of a hydrocarbon molecule. First, carbon monoxide is chemisorbed on the surface. This is reduced by hydrogen to the metallic carbide, Co_2C, or alternatively forms the carbide by reaction with another molecule of carbon monoxide. Molecular hydrogen then forms a $-CH_2$ group, still attached to the surface of the catalyst by a chemical bond. In the absence of chemisorbed hydrogen these methylene groups condense as macro-molecules or chains, still partially held to the catalyst surface by valence bonds in this transition state. Widely separated chemisorbed hydrogen atoms disrupt these macro-molecules and they are desorbed as hydrocarbon molecules. If chemisorbed hydrogen atoms are present in any great quantities then the chains will be short, in fact the majority of the methylene groups will be reduced to methane, rather than the higher hydrocarbons desired.

This series of reactions may be summarized as follows;-

i) $2Co + CO + H_2 \rightarrow Co_2C + H_2O$

ii) H_2 (mol,) $+ Co_2C \rightarrow 2Co + -CH_2$

iii) $x(-CH_2) \rightarrow (-CH_2)_x$

iv) hydrogenation cracking off of $(-CH_2)_x$ chain as an aliphatic hydrocarbon, saturated or olefinic.

v) if the catalyst surface is not largely Co_2C then chemisorbed hydrogen atoms will break off most of the methylene groups as methane as fast as they are formed.

Although no direct evidence that cobalt catalysts are capable of cracking hydrocarbons has been found, Craxford[4] shows that there is an optimum rate of synthesis gas flow over the catalyst bed, and postulates that at slower rates of flow the hydrocarbons produced in the first part of the bed are cracked in the later part to methane with consequent reduced yields. Craxford[4] further shows that the rate of formation of carbon dioxide steadily drops as the flow of synthesis gas is increased, showing no maximum, so that the formation of carbon dioxide cannot be connected directly with the synthesis reaction. The

reaction is probably:-

$$CO + 2H_2 \rightarrow H_2O + -CH_2$$

rather than:-

$$2CO + 2H_2 \rightarrow CO_2 + -CH_2 .$$

The experimental evidence on which Craxford bases this hypothesis is shown in Figure II. in graphical form.

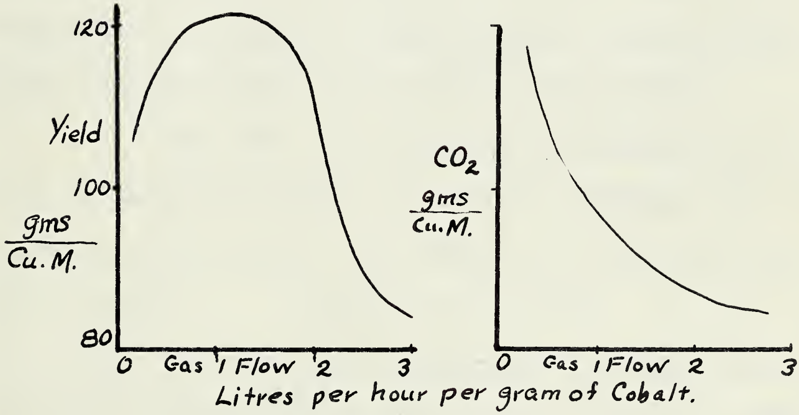


Figure II

Using this hypothesis as a basis, Craxford[5] then investigated the rate of carbiding of promoted and unpromoted catalysts in atmospheres of carbon monoxide alone and of synthesis gas. He tested five catalysts in all:-

i) Cobalt metal
ii) $Co:ThO_2$, 100:18
iii) Co:Kieselguhr , 1:1
iv) $Co:ThO_2:Kg$, 100:18:100
v) $Co:ThO_2:Kg$, 100:21:100

Of these, number (iv) was a successful synthesis catalyst but number (v) was inactive due probably to some uncontrolled factor in its preparation.

The rate of carbiding was slowest on the cobalt metal and fastest on cobalt promoted with the thorium oxide alone. The others in order of increasing rates were:- (iii), (v) and (iv).
The order was the same, (although the rates were faster) in the synthesis gas mixture as in carbon monoxide alone.

The rate of hydrogenation of ethylene was next measured over these five catalysts. All were found

to have substantially the same activity as hydrogenation catalysts.

The rate of reduction of the cobalt carbide was measured by admitting pure hydrogen to the carbided catalysts at 175° C. Cobalt alone, which had the slowest rate of carbiding, was found to have the slowest rate of reduction of the carbide also. Cobalt promoted with thorium oxide, which had the fastest rate of formation of the carbide, also had the greatest rate of reduction. The other three, which were the only ones that could be classified as useful catalysts, were in the reverse order:- (iv), (v) and (iii). in order of increasing rate of reduction of the carbide.

Thus it was shown that the most useful catalyst, number (iv), had the fastest rate of carbide formation combined with the slowest rate of carbide reduction among the useful catalysts. Catalyst number (v), which was not so successful, had a lower rate of carbide formation and a faster rate of carbide reduction. Number (iii), which is a rather poor catalyst for the synthesis reaction, was still slower in its rate of carbide formation and faster in its rate of reduction of the carbide.

This suggests an effective and relatively rapid method for testing the efficiency of synthesis catalysts. The combination of a rapid rate of carbide formation with a slow rate of reduction of that carbide should indicate a good catalyst.

EXPERIMENTAL.

I APPARATUS

The apparatus used was an adaptation of that design first proposed by Emmett for the study of adsorption. It is shown in Figure III. Storage bulbs, C,D,E,F, for the gases used in these measurements were connected by stopcocks, 3,4,5,6, to a vacuum line. This was connected through a stopcock, 1, to a McLeod gauge and through stopcock 2 to a Mercury diffusion pump backed by a rotary oil pump. Through stopcock 8 the line M,R was connected to the vacuum line and the gas storage bulbs. A mercury manometer, M, which could be evacuated through the stopcock 7, was used to measure the pressure inthis part of the system. A series of bulbs of known volume, I,II,III,IV,V, and the reaction chamber, R, (which could be surrounded by an electric furnace or vacuum flask) were connected to this manometer.

The volume of the line from the manometer to stopcocks 8 and 10 and the calibrated volumes, B, was calibrated, so that with the mercury level at known points between the bulbs, B, the volume of the system was accurately known.

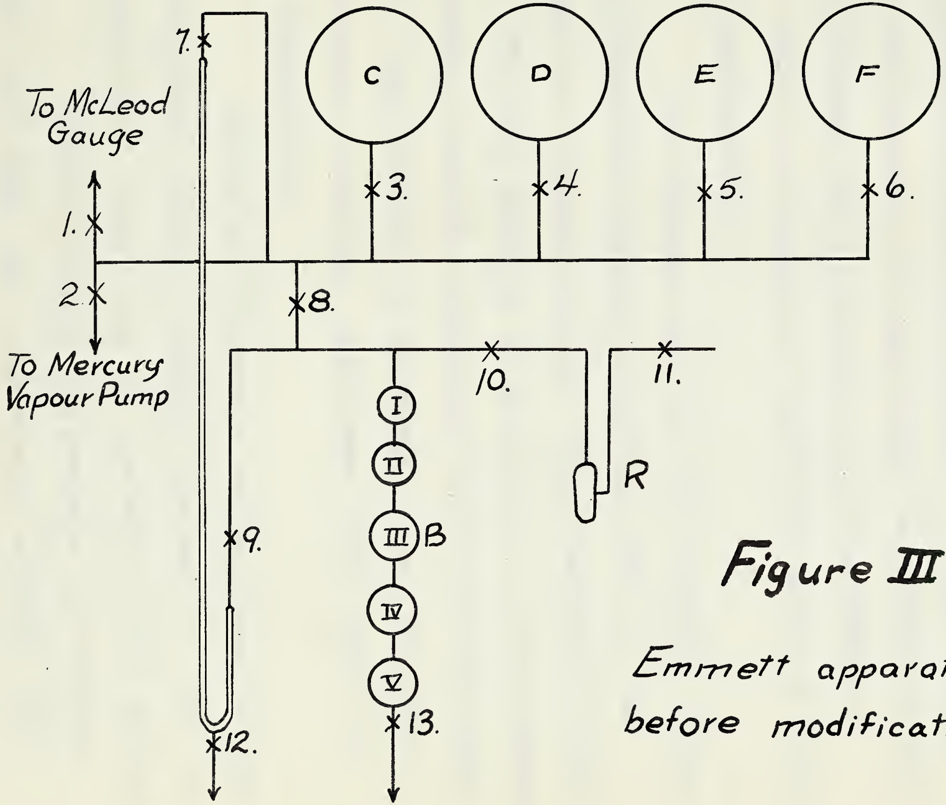

To McLeod Gauge
1.
2.
To Mercury Vapour Pump
7.
C
D
E
F
3.
4.
5.
6.
8.
9.
10.
11.
R
I
II
III
B
IV
V
12.
13.

Figure III

Emmett apparatus before modification

II PREPARATION OF GASES

The gases used were nitrogen, hydrogen, helium and carbon monoxide. Nitrogen was tank nitrogen passed through a liquid air trap to remove all condensible gases and vapours. It was recognized that small amounts of oxygen might be present in this tank nitrogen, but it was felt that the effect of this would not introduce a significant error in surface area measurements.

The hydrogen used was tank hydrogen, passed over platinized asbestos at 450° to 500° C., then through an activated charcoal trap immersed in liquid air. The only impurity of any account in tank hydrogen is oxygen, which is completely removed by this treatment. Small amounts of nitrogen, if not removed by the charcoal scrubber, would have little effect on the measurements.

Helium was commercial helium passed through an activated charcoal scrubbber immersed in liquid air. No appreciable impurities are present in such helium.

Carbon monoxide was prepared by dropping formic acid (85%) into concentrated sulfuric acid

(s.g. 1.85) at 100° C. The gas was passed through dehydrite and soda-lime tubes to absorb moisture and carbon dioxide, then through a glass wool packed trap immersed in liquid air. The only impurities present in carbon monoxide prepared in this manner are moisture and acid spray and a small amount of carbon dioxide, all of which will be completely removed by this treatment.

Each bulb in turn was evacuated, using the mercury vapour pump, and filled with one of these gases. Bulb C was filled with nitrogen, D with hydrogen, E with helium and F with carbon monoxide. The hydrogen system was so arranged that a continuous stream of purified hydrogen could be passed into the bulb D, and thence through stopcocks 4,8,10 and 11 over the catalyst for the reduction step.

III MODIFICATIONS

The apparatus as shown in Figure III was used for the first part of the investigation; the determination of adsorption isotherms and surface areas. The determination of the rate of carbiding and the rate of reduction of the carbide required a larger known volume of the reaction gas than could

be held in the bulbs B and also required that this gas could be circulated over the catalyst. Periodic measurement of the volume of gas remaining at known pressure or of the pressure at known volume was also necessary. It was still desired to carry out surface area measurements so that the design of the system must not be changed basically.

The first modification made with these requirements in mind was as shown in Figure IV. The large calibrated volume, Q, and stopcock 14 were added before the catalyst chamber and two connected bulbs, S, after it. Enough Dowtherm was in these two bulbs to fill one of them. With the Dowtherm level at stopcock 11 the volume was known; circulation was obtained by raising and lowering the mercury level in bulb Q with stopcocks 11 and 14 open; surface area measurements could be carried out by simply leaving bulb Q full of mercury.

After three runs had been made with this arrangement, discrepancies in the results obtained made it clear that this was not a satisfactory setup. The solubility of hydrogen and methane in the Dowtherm was tested by circulating these gases with no

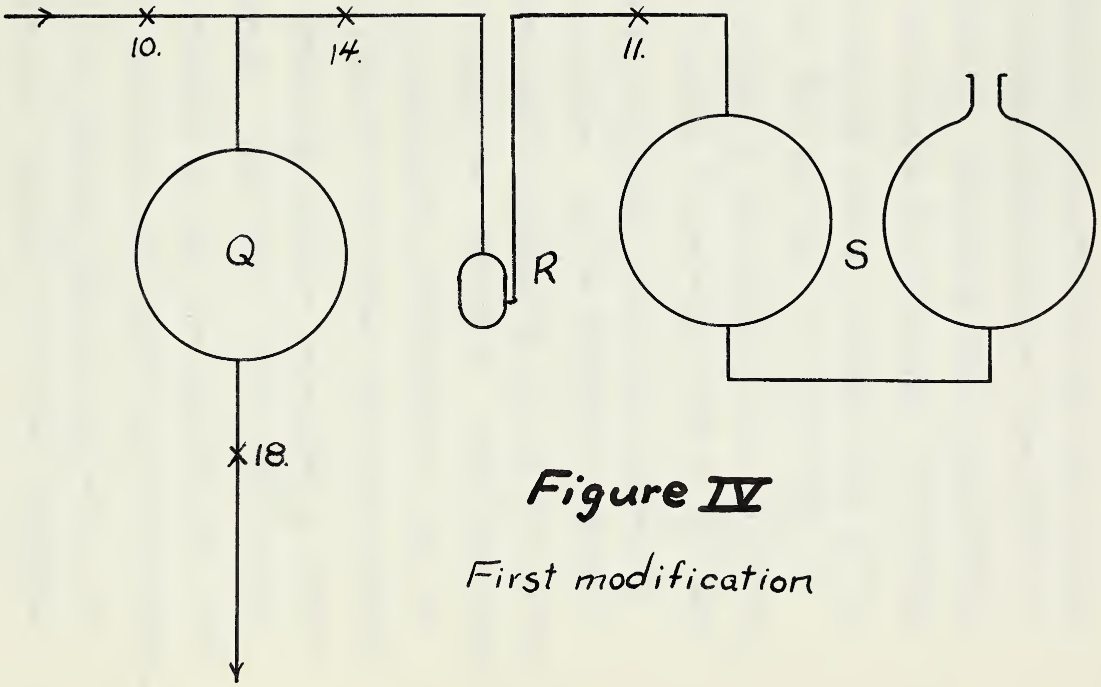
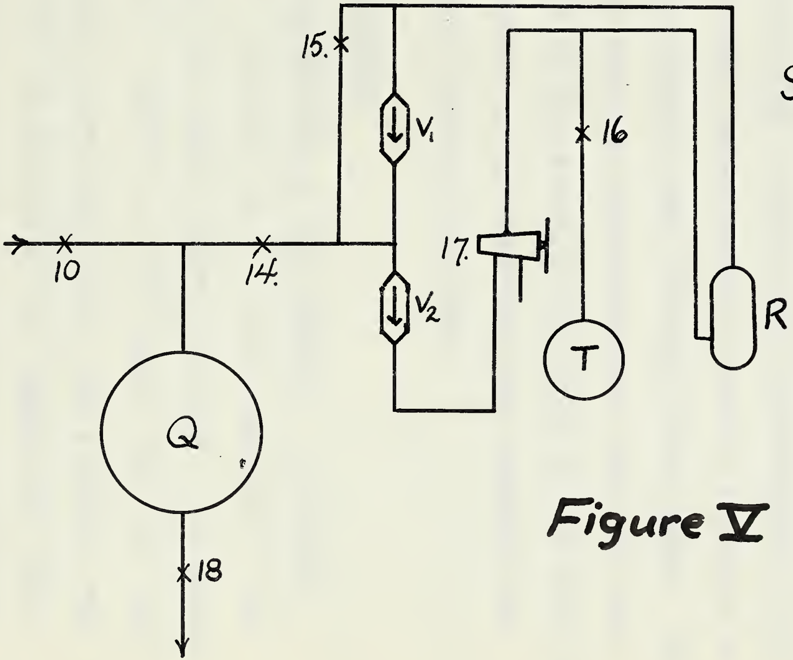

10.
14.
11.
Q
R
S
18.

Figure IV

First modification

catalyst in the system. It was found that hydrogen was not soluble but that methane was very soluble.

A second modification was then made as shown in Figure V. Two ground glass check valves, V_1 and V_2, were placed in the system, V_1 allowing gas to flow into the catalyst chamber only and V_2 allowing it to flow out only. A small bulb, T, added extra volume to the system to aid circulation. Raising and lowering the mercury level in the bulb Q with stopcock 15 closed and 14 open raised and lowered the pressure. As the pressure increased, gas was forced into R through V_1, and as the pressure decreased it flowed out through V_2. With the mercury level in Q at a known mark and stopcock 15 open to equalize the pressure the system had a known volume and the gas remaining could be determined by measuring the pressure. With bulb T closed off by stopcock 16 and stopcock 15 open the apparatus was still suitable for adsorption and surface area measurements. Reduction of the catalyst could be carried out by opening the two way stopcock 17 to the atmosphere and passing hydrogen through.


15.
V₁
V₂
10
14.
17.
16
T
R
Q
18

Second modification.
Circulating system
added.

Figure V

Two faults are inherent in this last design. First, the circulation is slow and somewhat uncertain; second, the pressure has to be varied about 16 cm. of mercury to give circulation. Since these are zero order reactions and not dependent on pressure or concentration, these two faults should not affect the results, providing a sufficient concentration of the reacting gas can be maintained over the catalyst to prevent the reaction from becoming first order. The pressure variation is accentuated by the fact that the products of the reaction are left in, so that the partial pressure of the reacting gas steadily decreases as the reaction procedes.

IV PROCEDURE

Preparation of the Sample:- A weighed sample of the catalyst to be tested was put in the chamber R and the whole sealed in place. The sample was degassed at 100° C. or 25° higher than the highest temperature to be used, until the pressure was less than 0.001 mm of mercury and would hold this with the mercury diffusion pump shut off (stopcock 2 closed). The time for this step varied from one

half hour for some keiselguhrs to two or three hours for some catalysts.

Measurement of the Dead Space:- Stopcock 10 was closed and a measured amount of helium taken in the bulbs B by opening stopcocks 5 and 8. With these stopcocks closed again the pressure in the bulbs was read on the manometer M. The temperature of the water bath around the bulbs was recorded.

The catalyst temperature was brought to the temperature of the measurement to be made by means of the electric furnace or a thermos flask containing an appropriate cooling agent. Stopcock 10 was opened, allowing the helium to expand into the reaction vessel. The new pressure was read on the manometer.

After the modification of the apparatus the only difference in this procedure was that stopcock 14 was used in place of stopcock 10.

Calculation of the dead space was made as follows:-

$$v_h = \frac{(P_1V_1 - P_2V_2)T_2}{T_1P_2(1+\alpha)}$$

where v_h is the volume of the dead space in R

P_1 is the pressure in bulbs B before expansion.

P_2 is the pressure in bulbs B after expansion.

V_1 is the known volume before expansion.

V_2 is the known volume after expansion.

T_1 is the temperature of the known volume.

T_2 is the temperature of the catalyst chamber R.

After the second modification, only the apparent dead space could be determined since only part of the system beyond stopcock 14 was at the temperature of the catalyst chamber. In this case then

$$v_h(\text{app.}) = \frac{P_1V_1 - P_2V_2}{P2} \quad \text{at temperature } T_1$$

A sample calculation for both v_h and v_h(app,) is shown:-

$V_1 = 16.43$ cc $\quad V_2 = 16.43$ cc

$P_1 = 76.73$ cm Hg $\quad P_2 = 36.30$ cm Hg

$T_1 = 23.5^\circ$ C $\quad T_2 = -190^\circ$ C (83° K)

$$v_h(\text{app}) = \frac{(76.73 \times 16.43 - 36.30 \times 16.43)}{36.30} = 18.30\text{cc}$$

$$v_h = \frac{(76.73 \times 16.43 - 36.30 \times 16.43) \times 83}{296.5 \times 36.30} = 5.12 \text{ cc}$$

The deviation of helium from the perfect gas law is negligible even at 83° K.

Determination of Surface Area:- The catalyst was degassed at 100° C. until a vacuum of at least 0.001 mm of mercury could be maintained with the mercury vapour pump shut off.

Stopcock 10 was closed and the chamber R was immersed in liquid air. A measured amount of nitrogen was taken in bulbs B by opening stopcocks 3 and 8. With these stopcocks closed again the pressure and temperature of the gas in the bulbs was recorded.

V_B is the volume of the bulbs and line containing the nitrogen.

P_B is the pressure in cm of mercury.

T_B is the temperature of the gas.

Stopcock 10 was opened and the new pressure recorded. The mercury level was varied in bulbs B to give several known volumes with corresponding pressures between 15 and 75 cm of mercury.

V_b is the known volume of bulbs and line to stopcock 10.

P_b is the pressure with stopcock 10 open.

The volume of gas adsorbed, V_{a_o}, at each equilibrium pressure, P_b, was determined from the relation

$$V_{a_o} = V_{B_o} - (V_{b_o} + V_{h_o})$$

where the subscript zeros indicate that the volumes concerned have been reduced to standard temperature and pressure. The variation of nitrogen from the ideal gas law at 83° K. must be taken into account.

Then P_b/P_o and $\frac{P_b}{V_{ao}/gm(P_o - P_b)}$ were calculated and plotted against one another. From the B.E.T. equation the slope of this plot is $(C-1)/(v_mC)$ and the intercept is $1/v_mC$. Then $v_m = \frac{1}{a+b}$ where "a" is the slope and"b" is the intercept. From v_m the surface area was calculated, assuming the area of the liquid nitrogen molecule to be 16.6 sq Å.

$$\text{Surface area} = \frac{v_m \times 6.02 \times 10^{23} \times 16.6 \times 10^{-20}}{22.4 \times 10^3}$$

A sample calculation is shown in Table I.

Measurement of Adsorption:- The procedure was identical with that described for the determination of the surface area. Calculations were carried only as far as v_{ao}/gm.

Reduction of the Catalyst:- Some surface area and adsorption measurements were made on reduced catalysts, and the reduction had to be carried out before determination of the rates of carbiding and reduction of the carbide.

TABLE I

T_b	P_b	V_b	V_{b_o}	V_{h_o}	V_{a_o}	$\frac{V_{a_o}}{gm}$	A	P_b/P_o
24.5	25.28	185.1	56.4	6.9	63.6	22.3	.0086	.160
24.6	31.34	133.5	50.4	8.4	68.1	23.8	.0104	.199
24.6	40.94	83.24	41.1	10.9	74.9	26.3	.0133	.259
24.6	50.90	50.34	30.9	13.6	82.4	28.9	.0165	.322
24.6	65.50	17.82	14.1	17.5	95.3	33.4	.0212	.414

Catalyst # 1(b)   Sample - 2.854 gms.

V_h = 5.90 cc. P_B = 56.84 cm. V_B = 185.1 cc

V_{B_o} = 126.9 cc. $A = \dfrac{P_b}{V_{a_o/gm}(P_o - P_b)}$

α = (for nitrogen at 83° K) 0.0455

TABLE II

Time	P_Q	T_Q	V_{Q_o}	$V_{h_o} + V_{Q_o}$	Vol. used	V/gm.Co
0	62.40	22.8°C	441.6			
16 min	52.42	23.0		419.9	43.4	43.4 cc
35 min	52.06	23.0		417.0	49.2	49.2
1 hr.	51.62	23.0		413.5	56.2	56.1
10 hrs	44.30	23.0		354.9	173.4	173.2

Catalyst # 7 Sample 4. Weight of sample - 3.003 gms.
Co in sample - 1.001 gms. V_Q = 583.1 cc.
V_h(app.) = 77.0 cc.

The catalyst chamber R was raised rapidly to 400° C. in an atmosphere of helium or nitrogen or evacuated. At this temperature hydrogen was passed over the catalyst in a rapid stream by opening stopcocks 4, 8, 10 and 11. After the first modification stopcock 14 was also open, and after the second modification, stopcocks 15 and 17 (to atmosphere). Bulb D was supplied constantly with purified tank hydrogen.

After two hours the catalyst was cooled in a slow stream of hydrogen, and kept in an atmosphere of hydrogen until the next step was to be carried out. The sample was in some cases stored in helium or evacuated but nitrogen was not used because of the possibility of contamination with oxygen. Nitrogen was used to determine the surface areas of reduced catalysts without apparent harm.

Measurement ofthe Rate of Carbiding:- After the reduction, the catalyst was evacuated at 225° C. to less than 0.001 mm of mercury and stopcock 14 closed. Bulb Q was filled with carbon monoxide by opening stopcocks 6 and 8. With these

stopcocks closed again the pressure and temperature of the gas was recorded, and the S.T.P. volume was calculated.

With the first modification, stopcock 14 was now opened, mercury run into bulb Q until the pressure was greater than atmospheric, stopcock 11 opened and the gas circulated back and forth over the catalyst. A reading was taken by lowering the mercury in Q, closing stopcock 11 when the Dowtherm level reached it, and reading the pressure and temperature of the gas remaining with the mercury level in Q at a known volume mark.

With the second modification, carbon monoxide was admitted to R by opening stopcock 14. With stopcock 15 closed and 17 in the circulating position the pressure was raised and lowered by raising and lowering the mercury level in Q. A reading was taken by lowering the level of mercury in Q to the known volume mark, opening stopcock 15 to equalize the pressure, and recording the temperature and pressure.

In both cases, from the known volume, temperature and pressure the volume of gas remaining

reduced to S.T.P. was calculated. Since the reaction is

$$2Co + 2CO \rightarrow Co_2C + CO_2$$

twice the volume which has disappeared represents the amount of carbon monoxide actually used up to that time.

Volume of carbon monoxide used per gram of cobalt in the sample was plotted against time. After ten hours the remaining gas was pumped off (to less than .001 mm) and stopcock 14 closed.

A sample run is shown in Table II.

Measurement of the Rate of Reduction of the Carbide:- This procedure was identical with that described for the measurement of the rate of carbiding. The temperature used was 175° C. and hydrogen was used in place of carbon monoxide. Again, since the reaction is :

$$Co_2C + 2H_2 \rightarrow 2Co + CH_4$$

the volume of Hydrogen actually used in the reaction is twice the apparent loss in volume.

RESULTS AND DISCUSSION.

I SURFACE AREAS

The surface areas of four different keiselguhrs were measured. The results are shown in Table III and Figures VI and VII. These measurements were made partly as a check on the apparatus. The surface areas of untreated catalyst keiselguhrs were known to be about 18 to 20 square meters per gram and those of alkali washed keiselguhrs to be about 2 square meters per gram. The values obtained are therefore reasonable.

It is apparent that the best support for a catalyst would most probably be Filter Cell because of its large surface area. A mild acid wash has no effect on its fine structure, since it has not changed the surface area.

The surface areas of six catalysts were measured in the unreduced state, as charged to the units. These results are shown in Table IV and in Figure VIII.

The first tested, shown as B.M., was a catalyst prepared by the U.S. Bureau of Mines and had the composition

$$Co:ThO_2:MgO:Kg - 100:6:12:200$$

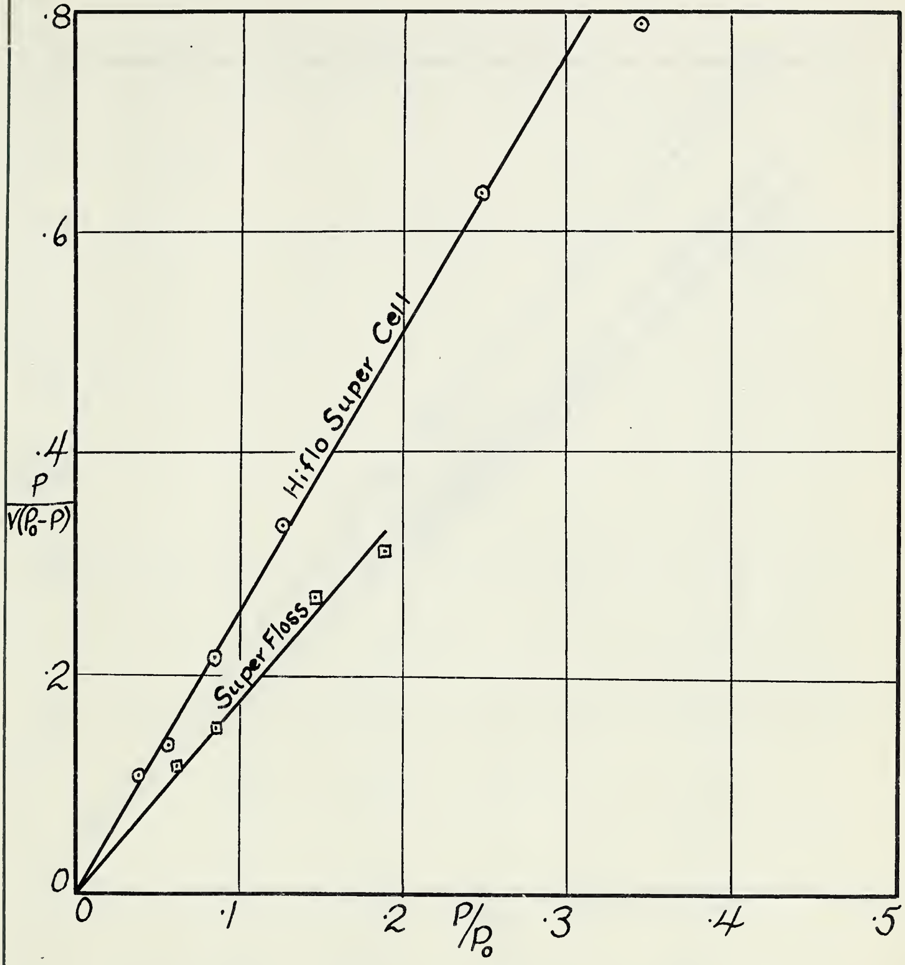


Figure VI

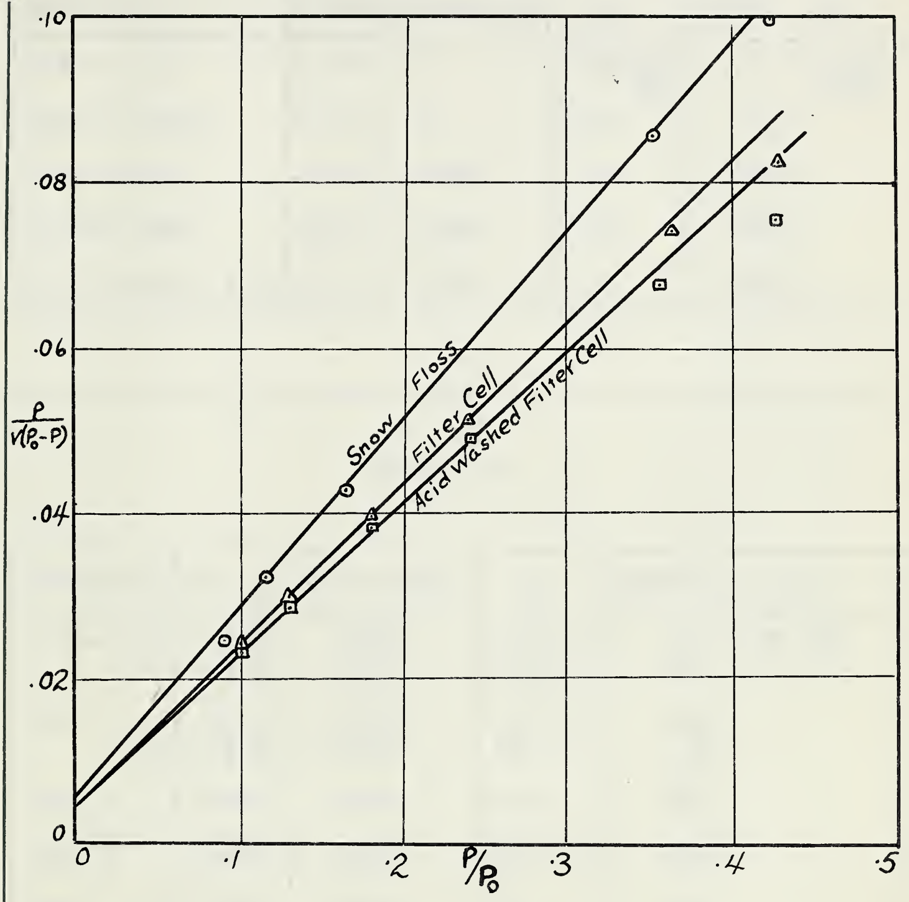

·10
·08
·06
·04
·02
0
$\frac{P}{V(P_0-P)}$
0
·1
·2
P/P_0
·3
·4
·5
Snow Floss
Filter Cell
Acid Washed Filter Cell

Figure VII

TABLE III

Material	Slope	Intercept	v_m	Surf. Area
Hiflo S.C.	2.54	0	0.39 $\frac{\text{cc}}{\text{gm}}$	1.7 $\frac{\text{Sq.M.}}{\text{gm.}}$
Super Floss	1.65	0	0.61	2.7
Snow Floss	.232	.0045	4.22	18.8
Filter Cell	.193	.0038	5.08	22.7
Acid Washed F.C.	.192	.0038	5.10	22.8

TABLE IV

Catalyst	Slope	Intercept	v_m	Surface Area
B.M. (a)	.0542	.0028	17.5	78 sq.M./gm
(b)	.0523	.0009	19.0	85
No. 1(a)	.0390	.0005	25.3	113
(b)	.0468	.0005	21.0	94
No. 2	.0276	.0005	35.5	158
No. 4	.0379	.0005	26.0	116
No.7 (a)	.0233	.0005	41.5	185
(b)	.0288	.0015	36.1	161

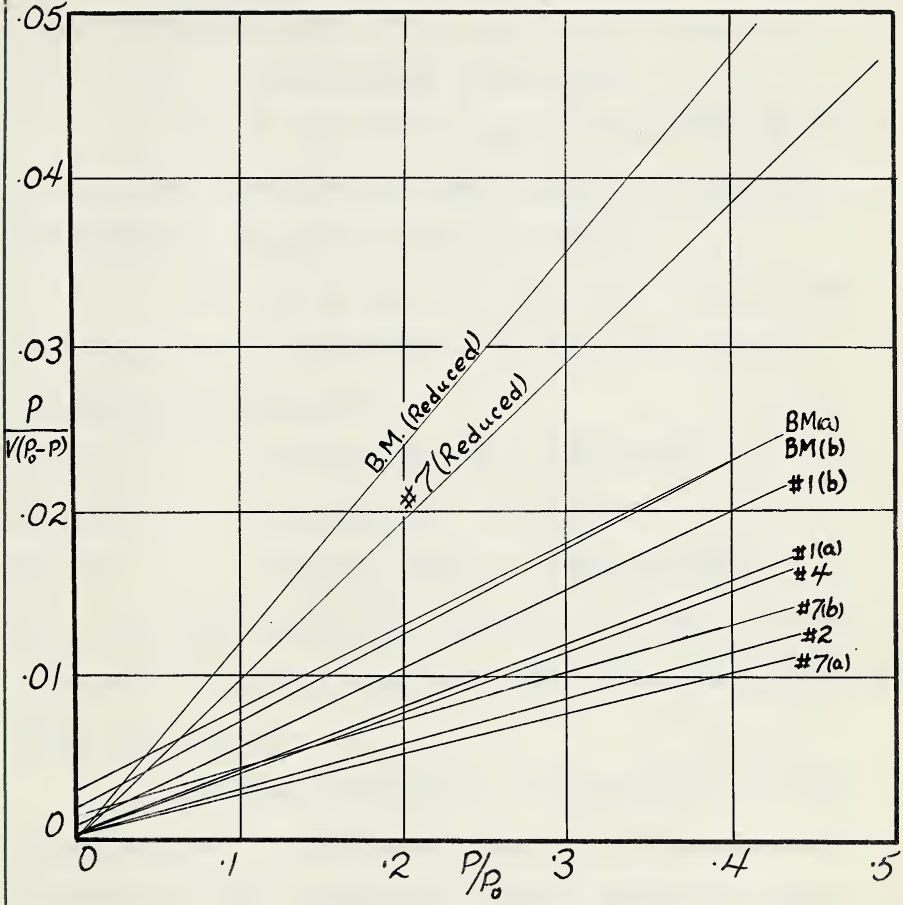

·05
·04
·03
·02
·01
0
P / V(P₀-P)
0
·1
·2
·3
·4
·5
P/P₀
B.M. (Reduced)
#7 (Reduced)
BM(a)
BM(b)
#1(b)
#1(a)
#4
#7(b)
#2
#7(a)

Figure VIII

No. 1 (a) was prepared by LaZerte, Loshaek and Scott[9] at the University of Alberta. in 1945. It had the composition

$$Co:ThO_2:Kg - 82:18:100$$

No. 1 (b) had the same composition as No. 1 (a) but was prepared one year later by Wright and Dimmock[10] at the University of Alberta.

Nos. 2, 4, and 7 (a and b) were also prepared by Wright and Dimmock in 1946 and had the following compositions

No. 2	$Co:ThO_2:MgO:Kg - 36:2:4:58$
No. 4	$Co:ThO_2:Kg - 100:18:100$
No. 7	$Co:ThO_2:MgO:Kg - 100:6:12:200$

No. 7 (a) was unpelleted and No. 7 (b) was pelleted once with 5% graphite added. All others were pelleted with 5% graphite.

Of these catalysts, probably No. 2 is the least active. Wright and Dimmock in a private communication have stated that yields were very small from this catalyst. On the other hand, No. 7, which has nearly the same surface area, is the most active of these catalysts when tested in the pilot plant units[10].

It is apparent , therefore, that surface area is not the controlling factor in catalyst activity. The surface areas of the catalysts tested are not in any comparable order to their activities.

The surface areas of catalysts B.M. (a) and No. 7 (b) were measured after reduction. These results are shown in Figure VIII and in Table V below.

TABLE V

Catalyst	Slope	Intercept	v_m	Surface Area
B.M.(red.)	.1183	0	8.46	38 sqM/gm
No.7(red.)	.0934	0	10.7	48

Emmett in a private communication reports little change in the surface area on reduction but these two catalysts show over 50% loss. It is possible that some oxidation of the catalyst is responsible although the greatest care was taken to avoid this.

II ADSORPTION

Several attempts were made to obtain reproducible results on the adsorption of carbon monoxide and hydrogen on B.M. catalyst. Since these are chemisorptions and only partially reversible with

pressure, each equilibrium point must be approached carefully from a point of lower adsorption.

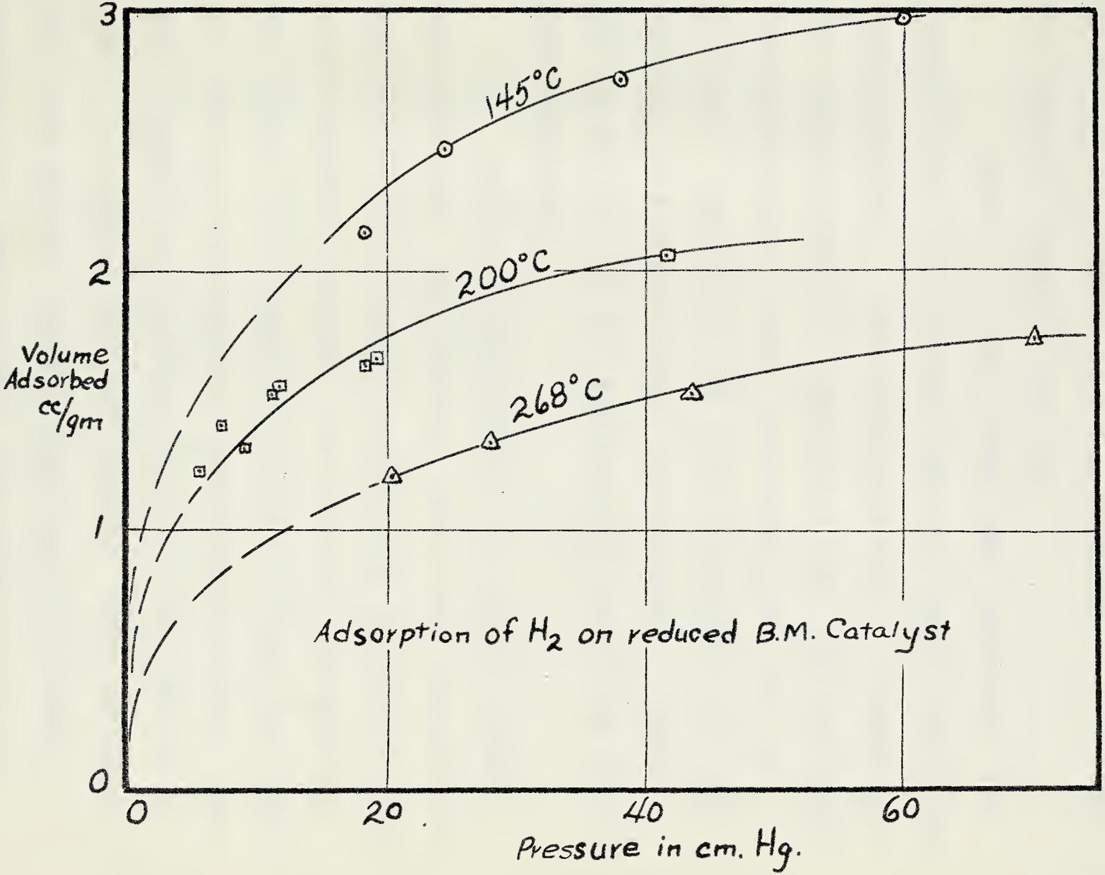
The only reproducible results that were obtained were for the adsorption of hydrogen on the reduced B.M. catalyst. These are shown in Figure IX.

In this case, the curves do not represent true equilibrium conditions since, even after eighteen hours, further adsorption could be detected at 200° C. and 42 cm pressure. Readings were taken after 10 minutes at the equilibrium pressure. Conditions were reasonably steady after this time and the points were reproducible within the limits of the accuracy of the experiment.

The difficulty of obtaining reproducible results and the slowness of the determination led to its abandonment. The adsorption of carbon monoxide on the reduced catalyst and of hydrogen on the carbided catalyst could not be measured and these were thought most likely to be significant.

III RATE OF CARBIDING AND REDUCTION OF THE CARBIDE

Catalyst #7, as a fairly successful catalyst, was tested for rate of carbiding and rate of reduction



3
2
1
0
Volume Adsorbed cc/gm
145°C
200°C
268°C
Adsorption of H_2 on reduced B.M. Catalyst
0
20
40
60
Pressure in cm. Hg.

Figure IX

of the carbide. Six samples in all were run, to obtain reproducible results if possible. The results are shown in Figures X and XI.

Runs 1, 2 and 3 show some measure of reproducibility in the rate; that is, their slopes are nearly parallel. Since Dowtherm was in contact with the reaction gases in these three runs and presumably dissolved some of them, the results are not significant. Similarly, the rate of reduction of the carbide for samples 2 and 3 is in error. Sample one was spoiled by the admission of air after three hours carbiding.

The last three runs, 4, 5 and 6, which were made after the Dowtherm bulbs were removed and replaced by the internal circulating apparatus, show little obvious agreement in the rates of carbiding. The slopes of the graphs of runs 4 and six are nearly the same but run 4 shows a much larger initial jump. Run 5 dropped off in rate after one hour but up to that point agreed well with run 6. After 10 hours runs four and six reached the same final state representing approximately 50% of the Co in the

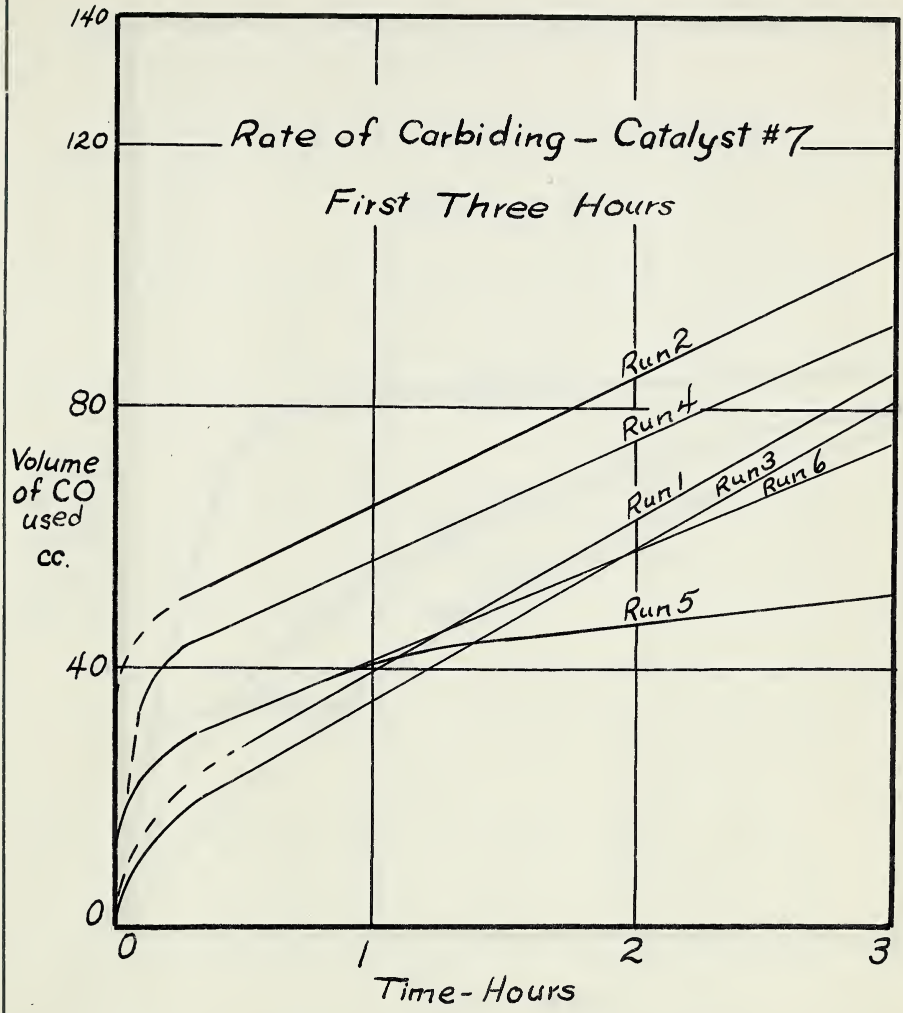

Rate of Carbiding – Catalyst #7
First Three Hours
Volume of CO used cc.
140
120
80
40
0
0
1
2
3
Time-Hours
Run 2
Run 4
Run 1
Run 3
Run 6
Run 5

Figure X

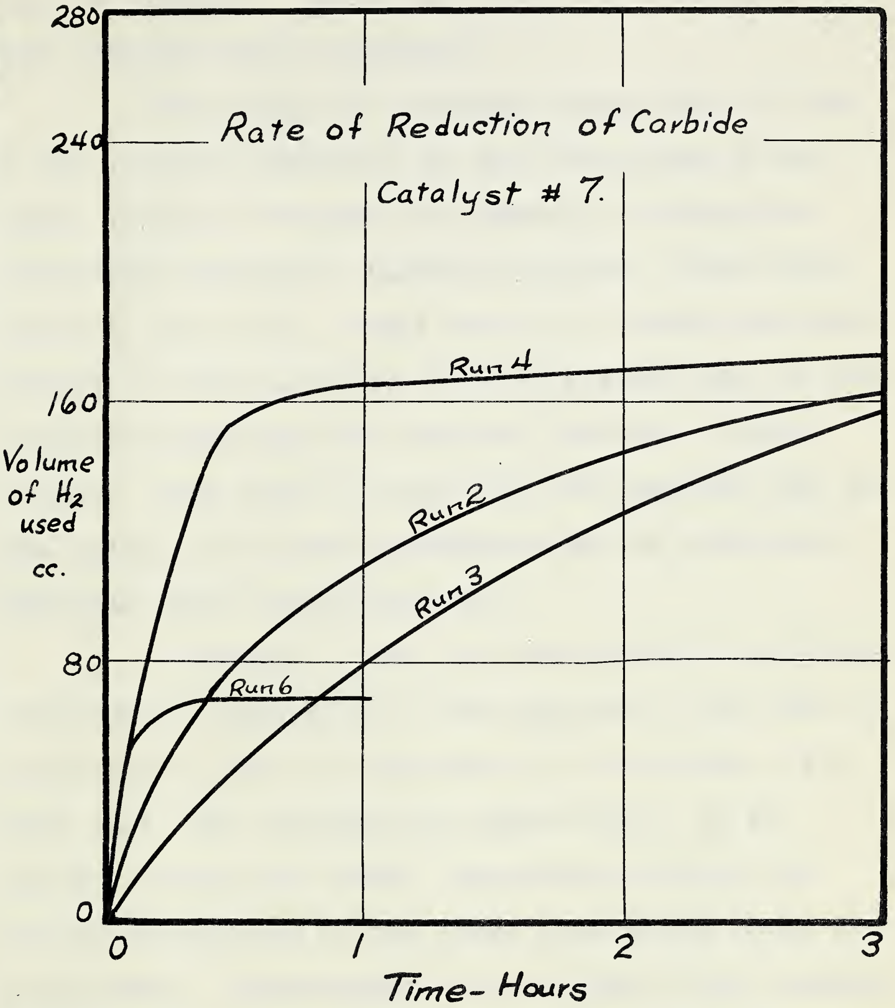

Rate of Reduction of Carbide
Catalyst # 7.
280
240
160
80
0
Volume of H_2 used cc.
Run 4
Run 2
Run 3
Run 6
0
1
2
3
Time- Hours

Figure XI

form of carbide. Run 5 was spoiled by admission of air after 10 hours carbiding.

The rates of reduction (Figure XI) of runs 4 and 6 are in agreement for the first part of the curve but run 6 dropped off suddenly in rate, after 30 minutes showing no further reaction. This would indicate that only a small amount of carbide had been formed, or more probably that the greater part of the carbide formed had been rendered inactive in some manner. Runs 2 and 3, made with the Dowtherm trap in the system, are lower presumably due to previously absorbed gases being given off.

Although it has not been possible to obtain reproducible results up to the present on the rate of carbiding or rate of reduction of the carbide, it is felt that this procedure has some value. It is probable that with better temperature control and faster circulation of the gases this method could be made useful. Measurement of the volume of gas remaining, at constant pressure, rather than the pressure at constant volume, would be faster and would not interupt the runs.

The most important factor in these measurements appears to be exact reproduction of the procedure in each run. Small differences in the reduction technique and subsequent storage of the catalyst overnight are suspected to affect the rates of carbiding and reduction of the the carbide to a considerable extent.

SUMMARY

The surface areas of several keiselguhrs were measured. The values obtained were of the proper order and it was possible to designate "Filter Cell" as the best catalyst supporter of those tested on this basis. Acid washing was shown to have no effect on the surface area of Filter Cell.

The surface areas of catalysts, unreduced and reduced, were measured and shown not to be the controlling factor in catalyst activity. Reduction of the catalyst was found to reduce the surface area substantially.

Adsorption of carbon monoxide and hydrogen on these catalysts was not measured successfully. No significant results could be obtained.

A method was evolved for the measurement of the rate of carbiding and the rate of reduction of the carbide on these catalysts. Reproducible results were not obtained but some correlation has been shown. With a perfected technique the method would probably prove successful.

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